



Separation of nickel(II), cobalt(II) and lanthanides from spent Ni-MH batteries by hydrochloric acid leaching, solvent extraction and precipitation

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ABSTRACT

The separation of nickel(II), cobalt(II) and lanthanides from chloride leach liquors of spent nickel-metal hydride (Ni-MH) batteries is described. After leaching in 12 mol L⁻¹ HCl, the traces of iron(III) and zinc(II) were extracted in a single stage with pure TBP (25 °C, A/O ratio = 1 v/v). Cobalt was extracted (93.6%) in two stages with Alamine 336 (10% vol. in kerosene, 25 °C, A/O = 1 v/v, free acidity = 4.3 mol L⁻¹). More than 98% of the lanthanides present in the raffinate were recovered through one of the following routes: (i) extraction with PC88A (20 vol.% in kerosene, 25 °C, A/O = 1 v/v, one stage, pH 1); (ii) precipitation as oxalates at pH 0.5. Nickel(II) was precipitated (>99%) as oxalate at pH 2. Metals separation in acidic medium avoids partial or total neutralization of the leachate and reduces the amount (and salinity) of the wastewater generated in the separation processes.

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1. Introduction

As a result of continuous technological innovations the number and variety of portable electronic devices have been growing worldwide, causing an increase of battery consumption for such devices (Provazi et al., 2011). Another consequence of this consumption profile is the generation of increasing amounts of waste electrical and electronic equipment (WEEE) (Bertuol et al., 2006). Therefore, the amount of spent batteries tends to increase with time. Since spent batteries are classified as hazardous wastes, their management is an important issue from the viewpoint of environmental and public health protection.

Nickel-metal hydride batteries (Ni-MH) are an example of typical rechargeable batteries. They have greatly replaced Ni-Cd batteries because of their technological and environmental advantages. The highly toxic cadmium was replaced by a mixture of metals (mischmetal), basically La, Ce, Pr and Nd, which are less harmful (Feng et al., 2006; Huang et al., 2011). These elements belong to the so-called rare earth elements which are widely used in modern technology (Lee et al., 2005; Rydha and Svärd, 2003). Cobalt and nickel have wide use in the manufacture of new materials for rechargeable batteries (Kumbasar, 2009; Rydha and Svärd, 2003; Swaina et al., 2008). In Brazil Ni-MH systems are an alternative to Zn-MnO₂ batteries as well as Li-based batteries, which are more expensive (Bertuol et al., 2006; Reddy et al., 2005). However, despite the replacement of cadmium by less toxic elements, spent Ni-MH batteries present environmental threats due to the presence of

high amounts of nickel, which is also a toxic element with various harmful effects (Rydha and Svärd, 2003; Tenório and Espinosa, 2002).

The processing of spent batteries is an important challenge not only from the viewpoint of treatment of a hazardous waste but also for the recovery of valuable elements from such wastes (Kao et al., 2006; Reddy et al., 2005; Yong-Feng et al., 2008). Due to the different metal compositions the spent Ni-Cd and Ni-MH batteries must be recycled separately (Barandas et al., 2007a, 2007b). Hydrometallurgical routes are the basis of processing spent Ni-MH batteries. In general, leaching with HCl or H₂SO₄ is the key step and the leachate is submitted to a combination of separation techniques (Bertuol et al., 2009; Provazi et al., 2011; Rabah et al., 2008; Souza et al., 2005). In some cases, toxic reagents such as sulfide ions are used for the precipitation of metal sulfides. On the other hand, solvent extraction (SX) has received much attention due to its advantages such as high selectivity and convenience for scale up (Sayar et al., 2009a). Separation of Ni(II) from Co(II) is not an easy task due to the similarity of the physico-chemical properties of their compounds. However, in comparison to Ni(II), Co(II) has a higher tendency to form stable complexes with ligands. For this reason SX of Co(II) appears to be an attractive method to separate these metal ions from the acidic leachates (Kumbasar, 2009).

Cobalt(II) can be extracted by amines in the presence of high Cl⁻ concentration (Ritcey, 1984). Free acidity and extractant concentration have a remarkable influence on Co(II) extraction (Filiz et al., 2006; Sayar et al., 2009a). When H₂SO₄ is the leachant, organophosphorus extractants have been employed (Li et al., 2009; Reddy et al., 2005, 2006; Zhang et al., 1999; Park et al., 2006). In these studies the pH is higher than in the original leachate, thus requiring a neutralization step. Extracted Co(II) can be stripped from the organic phase with solutions of inorganic salts such as NaCl, Na₂CO₃ and (NH₄)₂SO₄ (Sayar et al., 2009a). The use of amines as

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extractants has proven to be a good alternative for the extraction of Co(II) from synthetic solutions without making a significant change to the acidity or pH of the leachate (Ritcey, 1984; Sayar et al., 2009a).

The separation of lanthanides using SX has also been extensively studied. Organophosphorus extractants have been tested in chloride (Matsunaga et al., 2001; Morais and Ciminelli, 2004; Pietrelli et al., 2005; Tong et al., 2009), sulphuric (Jun et al., 1998; Fang et al., 2009) and nitric media (El-Nadi, 2010; Geist et al., 1999). Chelating extractants in acidic medium have also been tested for SX of lanthanum (Atanassova and Dukov, 2006). Extracted lanthanides can be stripped (>99%) from the organic after addition of NH_3 (pH 2–3) and oxalic acid (Vassura et al., 2009). Lanthanides can also be precipitated in sulphuric acid medium at pH<1.5 as $\text{NaLn}(\text{SO}_4)_2$ (~80 wt.% yield - Pietrelli et al., 2005). In chloride medium it is possible to recover these elements as oxalates (Barandas et al., 2007a, 2007b).

This work aims to test and propose a hydrometallurgical flowsheet to recover nickel, cobalt and lanthanides from hydrochloric acid leachates of spent Ni-MH batteries followed by (i) solvent extraction of Zn(II) and Fe(III), (ii) solvent extraction of Co(II), (iii) solvent extraction and precipitation of lanthanides as oxalate and (iv) precipitation of Ni(II) as oxalate.

2. Experimental

2.1. Samples and leaching procedure

A total of 120 spent Ni-MH batteries (~2,800 g) used in cell phones were used in this study. Their plastic cases were dismantled and the cells were cut longitudinally in order to separate the active components (anode, cathode, electrolyte) from the plastic pieces. The active components of all samples were mixed and fed into a milling machine for size reduction (100% <1 mm). The weight loss of the final material, mainly due to the vaporisation of moisture and other volatile compounds, was determined by drying the mass at 105 °C for 3 h to a constant value. The dried mass was leached with concentrated hydrochloric acid (12 mol L⁻¹) in a closed glass reactor equipped with a reflux condenser. The experiments were carried out at 40 °C (200 rpm) with a solid/liquid ratio of 150 g L⁻¹. After about 100 min all metallic parts were dissolved, producing a dark-green leachate. The insoluble matter (small plastic parts) was separated by filtration.

2.2. Solvent extraction (SX) procedures

The extractants employed were Alamine 336 (trioctyl/decylamine; Cognis Corporation) and PC88A (2-ethylhexylphosphonic acid, mono-2-ethylhexyl ester; Daihachi Chemical Co. Ltd). They were used without further purification. Deodorized aliphatic (>99%) kerosene (Exxon) was used as diluent. All SX experiments described below were performed at 25 °C with an aqueous/organic phase (A/O) ratio = 1 v/v (10 mL of each phase). After shaking for 5 min the system was left quiescent for 10 min for phase separation. If necessary, a second stage was performed using the raffinate under the same conditions used in the first stage. Experiments were run in triplicate and errors were always within ± 5%.

2.2.1. Extraction of Fe(III) and Zn(II) from leachate with pure TBP

Iron(III) and zinc(II) were extracted with pure TBP (Barandas et al., 2007a; El Dessouky et al., 2008) in order to avoid co-extraction with cobalt(II).

2.2.2. Extraction of Co(II) and Ni(II) from synthetic liquor and leachate with Alamine 336

Preliminary SX experiments were performed using synthetic CoCl_2 or NiCl_2 solutions. The effect of experimental parameters listed in Table 1 on solvent extraction was considered in the present study.

Table 1

Experimental parameters for cobalt(II) extraction with Alamine 336.

Co(II) (g L ⁻¹)	HCl (mol L ⁻¹)	Alamine 336 (mol L ⁻¹)
0.4–5	5	0.23 (10 vol.%)
4	8* to 10 ⁻⁵	0.23 (10 vol.%)
4	5	0.11–0.46 (5–20 vol.%)

*6 mol L⁻¹ NaOH was used to adjust free acidity. This means that the synthetic solution is a mixture of HCl + NaCl.

SX of Ni(II) with Alamine 336 was also studied using different concentrations of Ni(II) in the range 12–38 g L⁻¹. The experiments using Ni(II) synthetic solutions and the leachate were performed under the best free acidity and Alamine 336 concentration based on the results for Co(II) extraction from its synthetic solutions, described in Table 1.

2.2.3. Extraction of lanthanides with PC88A

Extraction of lanthanides was performed on the raffinate after Co(II) extraction with PC88A (20 vol.% in kerosene, 0.62 mol L⁻¹) with A/O ratio = 1 v/v at 25 °C. Free acidity was varied from its original value to 10⁻² mol L⁻¹ (pH 2) via addition of the appropriate amount of 6 mol L⁻¹ NaOH.

2.3. Precipitation of lanthanides and nickel as oxalate

After Co(II) extraction pH was adjusted to the range 0–4 via addition of 6 mol L⁻¹ NaOH. A solution of 0.3 mol L⁻¹ $(\text{NH}_4)_2\text{C}_2\text{O}_4$ was slowly added at 60 °C, under stirring (200 rpm), until the precipitation was completed. The fine solid was filtered and washed with 0.01 mol L⁻¹ $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (3 mL g⁻¹) and dried at 110 °C for 2 h.

2.4. Analytical methods

The composition of the solid after mixing, milling and drying the active components was determined by X-ray fluorescence (Shimadzu XRF 800HS). Calibration curves (0.1–1000 mg kg⁻¹) for Ni, Co, Mn, Fe, Zn and La were employed for quantitative analyses of these elements. As lanthanum is the most abundant lanthanide (Barandas et al., 2007a), it was considered as a representative of all lanthanides present in this solid. Concentration of metal ions in the leachate and aqueous phase after SX was determined by atomic absorption spectrophotometry, whereas lanthanum was determined by atomic emission spectroscopy (Shimadzu AA 6800). The concentration of metal ions in the organic phase was calculated by mass balance. The detection and quantification limits for the different metals were determined experimentally and were found to be, respectively: < 0.1 and 0.3 mg L⁻¹ [Co(II)]; < 0.01 and 0.01 mg L⁻¹ [Fe(III)]; < 0.1 and 0.1 mg L⁻¹ [Zn(II) and Ni(II)]; 0.2 and 0.5 mg L⁻¹ [Mn(II)]; 19 and 64 mg L⁻¹ [La(III)]. The pH measurements of aqueous solutions were conducted using a combination of a glass electrode and a Ag/AgCl reference electrode (Analab P500).

3. Results and discussion

3.1. Composition data

Table 2 presents the composition of the solid after mixing, milling and drying the active components of Ni-MH batteries. The composition of Ni-MH batteries (external case, polymers, active components) was presented elsewhere (Barandas et al., 2007a). Table 3 presents the concentrations of the metal ions in the corresponding leachate and their respective concentration after extraction with TBP. Data in both tables agree with literature data (Pietrelli et al., 2005; Rydha and Svärd, 2003; Vassura et al., 2009), except for lower iron content and higher volatiles present in the sample used in the present study.

Table 2

Chemical analysis of the active components of the Ni-MH batteries after mixing, milling and drying at 105 °C for 3 h.

Element	%	Element	%
Ni	26.4 ± 2.1	Fe	2.9 ± 0.2
Co	3.2 ± 0.6	Mn	1.3 ± 0.1
Y	0.3 ± 0.1	Zn	0.7 ± 0.1
La	8.9 ± 0.3	K	10.4 ± 0.2
Ce	2.3 ± 0.4	Na	3.7 ± 0.6
Pr	0.7 ± 0.1	Ca	0.7 ± 0.2
Al	0.3 ± 0.1	Others	0.6 ± 0.1
Loss of volatiles	37.6 ± 1.4		

3.2. SX of Co(II) and Ni(II) from synthetic solutions

3.2.1. Influence of metal concentration and free acidity

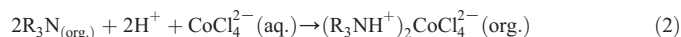
Fig. 1 shows that Co(II) extraction increased with the increase of Alamine 336 concentration. This result agrees with previous results with this amine (Filiz et al., 2006). The maximum workable amine concentration is 20 vol.% (0.28 mol L⁻¹). The formation of a third phase due to precipitation of the Co(II) salt and a remarkable increase in viscosity occurred at higher concentrations. Alamine 336 concentrations higher than 10 vol.% did not present a significant advantage in terms of %Co extraction. Therefore, the amine concentration was kept at 10% (v/v) for further experiments at different acidities.

The distribution coefficient, $D_{\text{Co(II)}}$, is defined as the ratio of metal concentration in organic phase to the metal concentration in aqueous phase at reaction equilibrium. The graph log D as a function of log [Alamine 336] (Fig. 2) shows that the slope is close to unity, thus suggesting a relationship 1 mol Alamine 336 to 1 mol Co(II), corresponding to the following reaction, under experimental conditions used in this study:



Fig. 3 shows that the increase of free acidity (above 2 mol L⁻¹) increased Co(II) extraction with Alamine 336. These results are consistent with literature data (Filiz et al., 2006; Sayar et al., 2009a, 2009b), although the effect is less pronounced above 5 mol L⁻¹. The extraction of Co(II) is due to the formation of anionic species (CoCl_3^- , CoCl_4^{2-}) with increasing amounts of chloride ions in solutions of HCl concentration higher than 2.5 mol L⁻¹ (Lister and Rosenblum, 1960; Morris et al., 1965; Sayar et al., 2009a). At pH 0 Co(II) was not significantly extracted, since the cationic species (Co^{2+} , CoCl^+) should predominate in this acidity range in chloride medium (Lister and Rosenblum, 1960; Wood, 1997).

The variation of log $D_{\text{Co(II)}}$ as a function of log [HCl] (Fig. 4) shows different behaviours according to the concentration of HCl. At higher concentrations (5.5–8 mol L⁻¹) the slope is close to 2 (Fig. 4A), suggesting the following reaction:

**Table 3**

Composition of leach liquor and extraction efficiency of Fe(III) and Zn(II) with pure TBP at 25 °C.

Metal ion	Concentration (g L ⁻¹)		% Extraction
	Before extraction	After extraction	
Co	4.7 ± 0.1	4.7 ± 0.1	0
Ni	39.6 ± 3.3	39.6 ± 2.6	0
La	18.0 ± 1.0	18.0 ± 0.5	0
Zn	1.0 ± 0.1	<0.01	>99.9
Mn	1.9 ± 0.1	1.9 ± 0.2	0
Fe	4.4 ± 0.3	0 ^a	100
Free acidity	5.5 mol L ⁻¹	4.5 mol L ⁻¹	18.2

a. Below the detection limit of the element (<0.01 mg L⁻¹, Section 2.4).

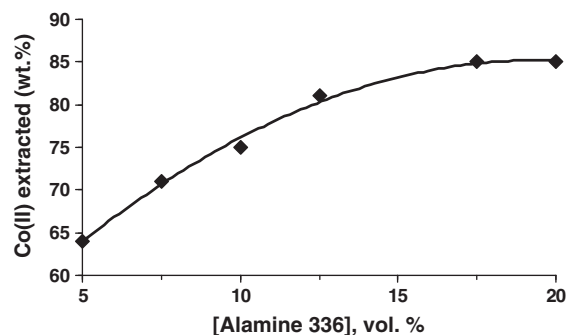


Fig. 1. Influence of Alamine 336 concentration on Co(II) extraction. [Co(II)] = 4.0 g L⁻¹, free acidity (HCl) 5 mol L⁻¹, one stage, A/O = 1 v/v.

At low concentrations in the range 4–5 mol L⁻¹ (Fig. 4) the slope is close to 1. This result agrees with the proposed reaction for cobalt extraction as a function of Alamine concentration (Fig. 2, Eq. (1)), since the free acidity was set at 5 mol L⁻¹. This behavior can be explained by the change of cobalt species distribution formed under different acidities and chloride concentrations (Lister and Rosenblum, 1960; Wood, 1997).

The increase of Co(II) concentration decreased the extraction yield (Fig. 5). This behaviour is consistent with the literature (Sayar et al., 2009a, 2009b) and can be attributed to the attainment of the maximum loading capacity of the solvent under the specified conditions (Marcus and Kertes, 1969).

Data on Fig. 6 show that 3.8% of Ni(II) was extracted from a solution of 48 g L⁻¹ Ni(II). When Ni(II) concentration was lower than 24 g L⁻¹, there was no significant extraction. Under comparable conditions, 60% of Ni(II) was extracted from a solution containing 3 g L⁻¹ (Sayar et al., 2009b) indicating the involvement of NiCl^+ and NiCl_2 species in solutions of higher concentrations of HCl (Butler, 1964; Lister and Rosenblum, 1960; Marcus and Kertes, 1969; Sayar et al., 2009a). Nickel(II) forms chlorocomplexes (NiCl_3^- , NiCl_4^{2-}) in HCl concentrations higher than 10 mol L⁻¹ (Morris et al., 1965; Sayar et al., 2009b).

3.3. Recovery of base metal ions from Ni-MH leachates

3.3.1. Extraction with pure TBP

The concentration of metal ions (g L⁻¹) in the leachate (Table 3) follows the order Ni(II) > La(III) > Co(II) ~ Fe(III) > Mn(II) > Zn(II). Previous researchers have recovered Fe(III) and Zn(II) using a SX step with pure TBP (Barandas et al., 2007a; El Dessouky et al., 2008). As shown in Table 3, after a single stage extraction using TBP at A/O = 1 (v/v) at 25 °C, more than 99.9% of Fe(III) and Zn(II) were removed, whilst other metal ions remained in the raffinate.

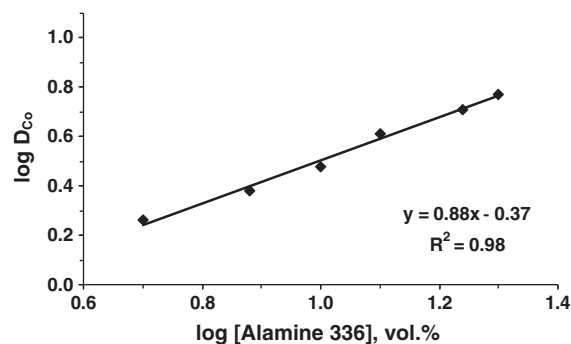


Fig. 2. Log D_{Co} versus log [Alamine 336] (free acidity 5 mol L⁻¹), based on the results of Fig. 1.

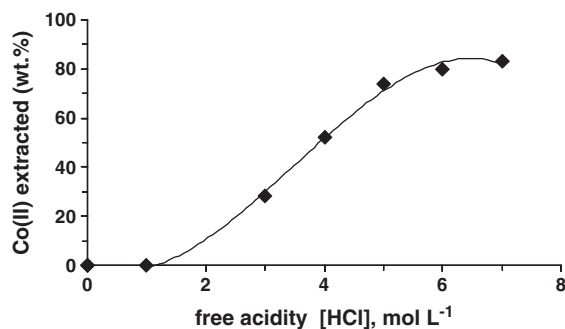
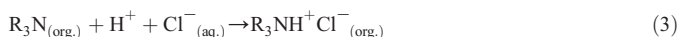


Fig. 3. Influence of the free acidity on Co(II) extraction with Alamine 336 (10 vol.% in kerosene). [Co(II)] = 4.0 g L⁻¹, one stage, A/O = 1 v/v, 25 °C.

3.3.2. Extraction with Alamine 336

In a single stage extraction with Alamine 336, 60% of Co(II) was extracted from the raffinate described in Section 3.3.1. Nickel(II) and lanthanides were not significantly extracted (Table 4). Taking into account the initial free acidity of the leachate (5.5 mol L⁻¹) this result agrees with data obtained with synthetic Co(II) and Ni(II) solutions (Figs. 5 and 6). After a second stage, 93.6% of Co(II) and 2.8% of Ni(II) were extracted (Table 4). This leads to a separation factor ($D_{\text{Co(II)}}/D_{\text{Ni(II)}}$, Sayar et al., 2009a) of about 500. Sayar et al. (2009a) achieved a higher extraction of 10–20% under similar conditions. The overall cobalt recovery of 94% is comparable to data for element recovery from spent NiCd and Ni-MH battery leachates using organophosphorus extractants (Li et al., 2009; Reddy et al., 2005, 2006), but without changing much the free acidity of the leachate.

The decrease of the free acidity from 4.5 to 4.3 (after one stage) and 3.0 mol L⁻¹ (after two stages) can be explained by some co-extraction of HCl by Alamine 336 (Sarangi et al., 2004):



3.4. Recovery of lanthanides

3.4.1. Via extraction with PC88A

The extraction of lanthanides by PC 88A (20 vol.% in kerosene) was unsuccessful due to the high free acidity of the leachate (5.5 mol L⁻¹). Furthermore, after Co(II) extraction, under a lower acidity of the raffinate (4.3 or 3.0 mol L⁻¹) no lanthanides were extracted by Alamine 336 (Table 4). The acidity was further reduced by partial neutralization with NaOH to 0.1 or 0.01 mol L⁻¹ HCl (pH 1 or 2, respectively). This facilitated the extraction of more than 99.9% of lanthanides in two stages

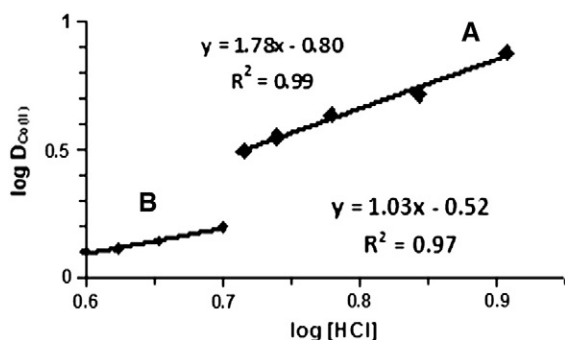


Fig. 4. Log $D_{\text{Co(II)}}$ versus log $[\text{H}^+]$, based on the results of Fig. 3.

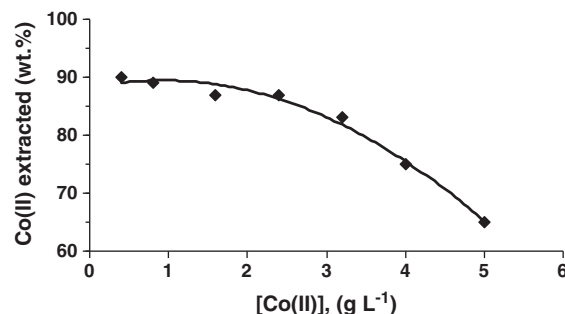
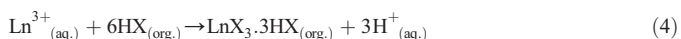


Fig. 5. Extraction of Co(II) from synthetic CoCl₂ solutions with Alamine 336 (10 vol.% in kerosene). Free acidity (HCl) 5 mol L⁻¹, one stage, A/O = 1 v/v, 25 °C.

(Table 5) without interference from Ni(II), Mn(II) and remnant Co(II). The extraction of lanthanides by PC88A can be described by the following equation (Morais and Ciminelli, 2004; Pietrelli et al., 2002):

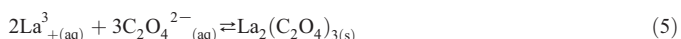


At pH 2 some Mn(II) precipitated as a brown solid (probably MnO₂), that was filtered before extraction. However, in this pH, 5.7% Ni(II) and 5.5% of Mn(II) were co-extracted (Table 5).

Lanthanides were easily stripped by 0.5 mol L⁻¹ HCl in one stage at 25 °C (A/O = 1 v/v). They may also be directly precipitated as oxalates (Barandas et al., 2007a). The results from this work are different from those of Morais and Ciminelli (2004), who found lower extraction yields (below 20%) despite the use of a higher PC88A concentration (45 vol.%). However, stripping efficiency was comparable in both studies.

3.4.2. Via precipitation with ammonium oxalate

pH plays a critical role on lanthanide precipitation as oxalate. The reactions for oxalate precipitation are described by Eq. (5) and (6) (Feigl, 1958; Lurie, 1978)



$$K_{\text{sp}}\text{La}_2(\text{C}_2\text{O}_4)_3 = 2.5 \times 10^{-37}, S = (K_{\text{sp}}/108)^{1/5} = 2 \times 10^{-8} \text{ mol L}^{-1}$$

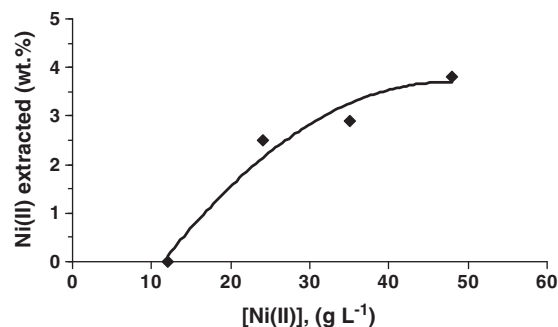


Fig. 6. Extraction of Ni(II) from synthetic NiCl₂ solutions with Alamine 336 (10 vol.% in kerosene). Free acidity (HCl) 5 mol L⁻¹, one stage, A/O = 1 v/v, 25 °C.

Table 4
Extraction efficiency of Co(II) and Ni(II) with Alamine 336*.

Metal ion	[M] (g L ⁻¹)	[M] (g L ⁻¹) after one stage	% Extraction	[M] (g L ⁻¹) after two stages	% Extraction
Co	4.7 ± 0.1	1.9 ± 0.1	60.0	0.30 ± 0.02	93.6
Ni	39.6 ± 2.6	39.6 ± 2.1	0	38.5 ± 2.3	2.8
La	18.0 ± 0.5	18.0 ± 0.9	0	18.0 ± 1.0	0
Mn	1.9 ± 0.2	1.9 ± 0.1	0	1.9 ± 0.1	0
Free acidity	4.5 mol L ⁻¹	4.3 mol L ⁻¹	–	3.0 mol L ⁻¹	–

*10 vol.% in kerosene, A/O = 1 v/v, 25 °C after one or two stages.

$$K_{sp} \text{NiC}_2\text{O}_4 = 4 \times 10^{-10}, S = (K_{sp})^{1/2} = 2 \times 10^{-5} \text{ mol L}^{-1}$$

where S = solubility of $\text{La}_2(\text{C}_2\text{O}_4)_3$ or NiC_2O_4 in mol L^{-1} . The calculated values based on K_{sp} show that $S_{\text{Ni oxalate}}$ is 1000 times higher than $S_{\text{La oxalate}}$. Therefore, $\text{La}_2(\text{C}_2\text{O}_4)_3$ tend to precipitate before NiC_2O_4 , allowing a selective fractional precipitation of lanthanides from a solution containing lanthanides and nickel(II).

The acidity also plays a critical role on lanthanide precipitation as oxalate. The lanthanides precipitation began at pH 0 but the yield was low (50%). The effect of pH summarized in Table 6 indicates that at pH 0.5, lanthanides recovery reached 98.5%, without interfering elements. At pH 1, the recovery surpassed 99.5% but Mn(II) was also partially precipitated (10%). At pH 2 the amount on impurities sharply increased: 25% Mn(II), 23% Ni(II) and all remaining Co(II) not extracted by Alamine 336 co-precipitated.

Despite its simplicity, selective precipitation of lanthanides as oxalate requires a much more rigid control of experimental parameters. The yield was somewhat lower to recover these elements with high purity. Therefore, SX appears to be a better choice for recovering lanthanides from Ni-MH leachates.

3.5. Nickel recovery

More than 99.5% of the nickel present in the raffinate after lanthanide extraction with PC88A was recovered as oxalate at pH 2. This corresponds to 97% of the overall element present in the original leachate. The remnant Co(II) not extracted by Alamine 336 and all Mn(II) were also recovered as oxalate. The yield and the composition of precipitate did not change at pH higher than 2. However, Mn and Co accounts for less than 4 and 1% of the metals present in the solid, respectively (Table 7). For pH values lower than 1 Ni(II) precipitation was not observed, while partial precipitation occurred from solutions of pH 1–2.

Table 5
Effect of acid on metal ion extraction with PC88A.

Metal ion	[M] (g L ⁻¹)	Free acidity (mol L ⁻¹)	[M] after one stage	[M] after two stages	Total extracted after two stages (%)
La	18.0 ± 1.0	0.1	7.3 ± 0.2	0 ^a	>99.9
		0.01	6.3 ± 0.3	0 ^a	>99.9
Ni	38.5 ± 2.3	0.1	38.5 ± 2.1	38.5 ± 2.0	0
		0.01	38.4 ± 1.9	36.3 ± 2.0	5.7
Mn	1.9 ± 0.1	0.1	1.9 ± 0.1	1.9 ± 0.01	0
		0.01	1.9 ± 0.3	1.8 ± 0.4	5.5

a. Below the detection limit of the element (19 mg L⁻¹, Section 2.4).**Table 6**
Precipitation efficiency of metal ions as oxalate at pH 0–2.

Metal ion (M)	La	Ni	Co	Mn
Concentration (g L ⁻¹) before precipitation	18.0 ± 1.0	38.5 ± 2.3	0.30 ± 0.02	1.9 ± 0.1
Concentration (g L ⁻¹) after precipitation				
pH 0	9.01 ± 0.26	38.5 ± 2.4	0.30 ± 0.02	1.9 ± 0.1
pH 0.5	0.28 ± 0.06	38.5 ± 2.3	0.30 ± 0.06	1.9 ± 0.2
pH 1	0 ^a	38.5 ± 2.0	0.29 ± 0.03	1.7 ± 0.1
pH 2	0 ^a	29.6 ± 0.9	0 ^a	1.4 ± 0.3
% Precipitated				
pH 0	50	0	0	0
pH 0.5	98.5	0	0	0
pH 1	>99.9	0	0	10
pH 2	>99.9	23	100	25

a. Below the detection limit of the element (see Section 2.4).

3.6. Proposed flowsheet

Fig. 7 presents the complete flowsheet, from the Ni-MH battery dismantling to nickel recovery as oxalate.

4. Conclusions

The extraction of Co(II) follows a 1:1 molar stoichiometry with Alamine 336. Tertiary amines appear to be good extractants for Co(II) in high HCl concentrations. The milled and dried active components of spent Ni-MH batteries were leached with 12 mol L⁻¹ HCl at 40 °C for 100 min. Pure TBP (A/O ratio = 1 v/v, 25 °C, one stage) extracted Zn(II) and Fe(III) from the leachate. From the raffinate, 93.6% of Co(II) was extracted with Alamine 336 (10 vol.% in kerosene) in two stages (free acidity 4.3 mol L⁻¹, A/O ratio = 1 v/v, 25 °C) along with 2.8% Ni (II).

Lanthanides were extracted (>99.9%) in two stages with PC 88A (20 vol.% in kerosene, A/O ratio = 1 v/v, 25 °C) at pH 1. Higher pH lead to some co-extraction of Mn(II) and Ni(II), whereas at pH 0 no extraction took place. Precipitation of lanthanides with ammonium oxalate at pH 0.5 gave a high purity final product but the yield was slightly lower (98.5%). As the pH was increased from 1 to 4, the amount of metal impurities sharply increased. Thus, solvent extraction appears to be a better separation method for lanthanide recovery with high purity and yield. Although Ni(II) was successfully precipitated as oxalate at pH 2, the non-extracted Co(II) and Mn(II) were also present in reasonable amounts in the precipitate, thus requiring additional purification steps.

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Table 7
Precipitation efficiency of metal ions as oxalate at pH 2–4.

Metal ion (M)	Ni	Co	Mn
[M] after lanthanide precipitation, pH 1	38.5 ± 2.0	0.29 ± 0.03	1.7 ± 0.1
[M] after Ni precipitation, pH 2	0.19 ± 0.01	0 ^a	0.01
[M] after Ni precipitation, pH 3	0.15 ± 0.02	0 ^a	0 ^a
[M] after Ni precipitation, pH 4	0.11 ± 0.01	0 ^a	0 ^a
% precipitated at pH 2	99.5	100	99.4
% precipitated at pH 3	99.6	100	100
% precipitated at pH 4	99.7	100	100

a. Below the detection limit of the element (see Section 2.4).

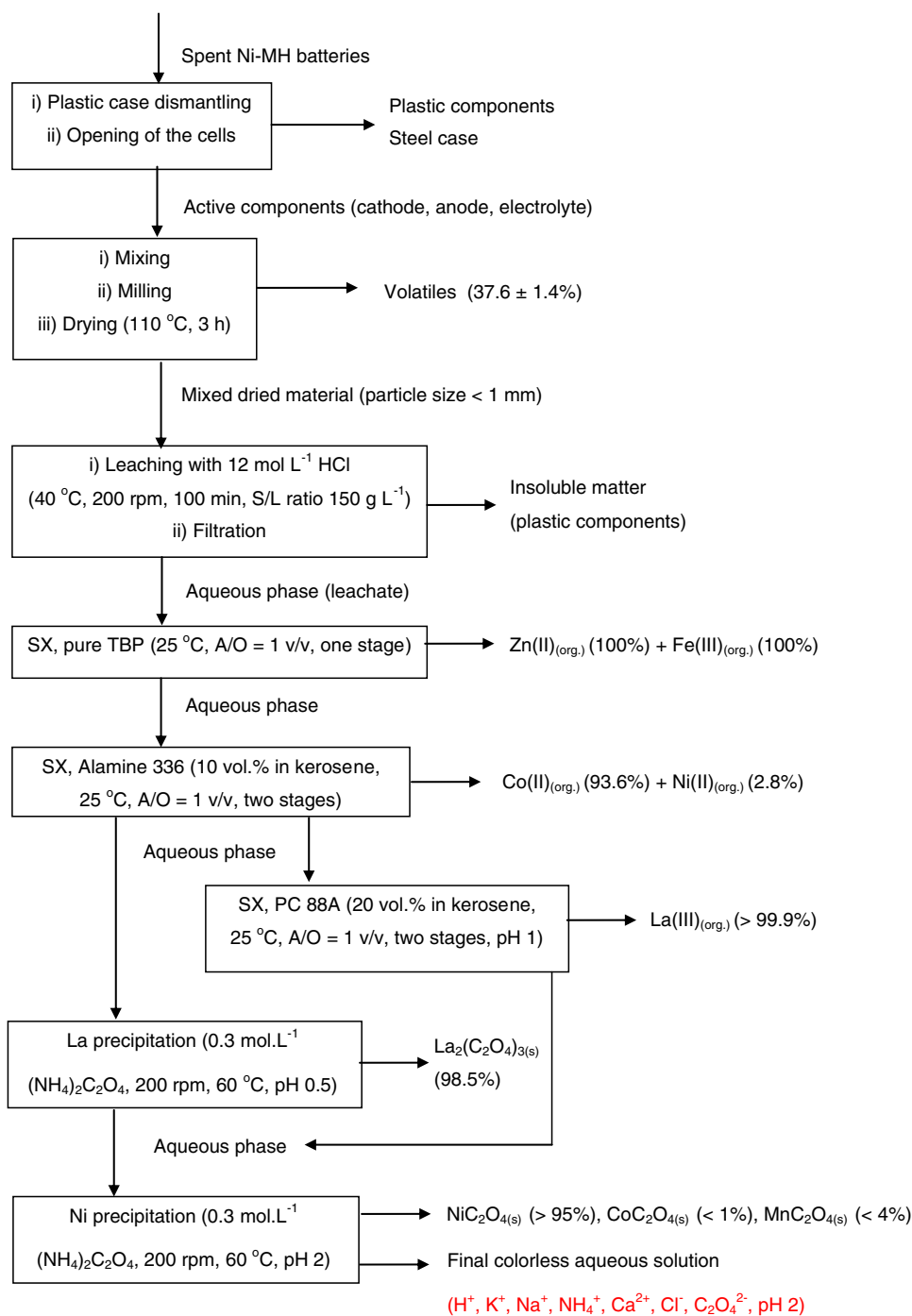


Fig. 7. Flowsheet of the metals separation from the active components of spent Ni-MH batteries.

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